

Desulphurization of odorous gases of a pulp mill**1AP20Rsc&UPT/PTO 31 MAR 2006**

The present invention relates to a method according to the preamble of claim 1 for the desulphurization of the circulation of chemicals in a sulphate pulp mill.

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According to a method of this kind, concentrated odorous gases of the process streams in sulphate processes, which gases contain sulphur compounds, are collected and these odorous gases are combusted in order to oxidize the sulphur compounds.

10 1 The invention further relates to the use according to claim 19 and arrangement according to the preamble of claim 20.

The circulations in modern pulp mills are closed so that, although non-sulphurous chemicals are substituted for sulphur-containing fresh chemicals, the circulation must be 15 desulphurized to prevent uncontrollable sulphur emissions. All modern sulphate pulp mills burn concentrated odorous gases either in soda recovery boilers, lime sludge reburning kilns or in separate odorous gas boilers or reserve flames.

20 2 When the concentrated odorous gases are burnt in the soda recovery boiler, sulphur is removed either by flue gas emissions (sulphur dioxide) or in the form of pulverized fuel ash. Generally, pulverized fuel ash is discharged from the system by releasing it into the river and lake system. Sulphur dioxide-containing flue gas emissions cause acidification of soil, damages to the trees and to the surface materials of buildings, and other environmental damages. Ash, in turn, contains abundantly wood-based heavy metals; 25 therefore, it is possible that the release of pulverized fuel ash into the water system will in the future be prohibited on environmental grounds. A further considerable disadvantage related to the removal of pulverized fuel ash is that, along with sulphur, also sodium in a molar ratio of Na/S 2/1 contained in the ash exits, and must then be added to the system.

30 3 When concentrated odorous gases are combusted in the lime sludge reburning kiln, the sulphur either exits as flue gas emission (sulphur dioxide and TRS = total reduced sulphur, i.e., so-called smelly sulphur compounds) or in waste lime/waste lime sludge. In addition to the above disadvantages, sulphur also causes running failures (cycles, among others) in the lime sludge reburning kiln.

When concentrated odorous gases are burnt in the separate odorous gas boilers, either sodium bisulphite or a dilute sulphur dioxide solution is obtained. In sodium bisulphite, sodium in a ratio of Na/S = 1/1 exits the system along with the sulphur.

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When burning concentrated odorous gases in the reserve flame, all sulphur escape as air emission in the form of sulphur dioxide.

All desulphurization methods currently used have one or more of the following
10 disadvantages: emissions into the air increase, losses of sodium increase, whereby the operating expenses grow because of the substitution chemical needed, or the end product obtained in the desulphurization is useless to the mill.

It is an object of the present invention to eliminate problems related to known technology
15 and to provide a completely new solution for recovering sulphur from the process streams of a sulphate process.

The present invention is based on the idea that the sulphur contained in concentrated odorous gases is recovered as elemental sulphur which can be returned to the process or
20 which can be employed in other practical applications.

Selective oxidation of sulphur compounds into elemental sulphur is previously known in the art. Accordingly, US 4,522,746 discloses the treating of sulphur-containing gas flow by converting essentially all sulphur compounds in the gas flow first to hydrogen sulphide and
25 oxidation of hydrogen sulphide into elemental sulphur at low temperature (160 – 320 °C) in the presence of titanium dioxide catalyst. FI Patent Specification No. 102250 discloses a catalyst for the selective oxidation of sulphur compounds into elemental sulphur, a method for preparing the catalyst, and a method for the selective oxidation of sulphur compounds into elemental sulphur. Published FI Patent Application No. 903673, in turn,
30 suggests monolithic catalysts for the treatment of sulphur compounds-containing gases in the industry. Published FI Patent Application No. 933481 discloses a method and an arrangement for the treatment of black liquor originating from a sulphate process for the recovery of energy and chemicals. Hydrogen sulphide can be produced from exhaust gas

containing sulphur compounds when heating the black liquor. Hydrogen sulphide can be used for different purposes, for example it can be oxidized into elemental sulphur.

5 The published GB Patent Application No. 2117749 describes a method and an apparatus for the combustion of gases containing hydrogen sulphide to form elemental sulphur.

None of the above solutions suggests the treatment of concentrated odorous gases; neither do they contain any suggestions for the recycling of the sulphur thus obtained.

10 According to the invention, the odorous gases collected from the process streams of the sulphate pulp mill are combusted at a low air index so that at least an essential part of the sulphur compounds is oxidized into elemental sulphur, which is removed from the system. This solution can be used to remove sulphur from the waste gases of the pulp mill in a controllable way. The method of oxidation of sulphur compounds used in the invention is
15 based on the so-called Claus process.

The invention also provides an arrangement for the removal of sulphur from the circulation of chemicals of a sulphate pulp mill, comprising a combustion unit for the odorous gases, which is provided with an inlet, which is connected to the source of concentrated odorous
20 gases, and with an outlet, through which the oxidized sulphur compounds of the concentrated odorous gases can be removed from the device as elemental sulphur. The combustion unit according to the invention comprises at least one combustion device of the Claus system.

25 More specifically, the method according to the invention is mainly characterized by what is stated in the characterizing part of claim 1.

The use of the Claus process according to the invention is described in claim 19.

30 The arrangement according to the invention is, in turn, characterized by what is stated in the characterizing part of claim 20.

The invention provides considerable advantages. Accordingly, the method can be used to desulphurize the waste gases of the sulphate pulp mill in particular. The sulphur of the odorous gases is recovered in a form that can be utilized in the same or in other processes.

5 The methods according to known technology provide no solutions, which, according to the invention, would integrate the method of desulphurization into the exhaust system of odorous gases of a sulphate cellulose mill.

To optimize the discharge of elemental sulphur in various temperature ranges, the
10 combustion of odorous gases can be carried out in one or more steps. This can be carried out so that one or more combustion units of the Claus system are arranged sequentially. Various running conditions can be used therein.

On the other hand, the invention can be used for converting sulphur, for example, so that it
15 can be exploited by combusting sulphur to sulphur dioxide which can be used in bleaching, and to make sulphuric acid by means of processing either for the manufacture of bleaching chemicals or for peeling pine oil. At the same time, the sodium losses of the mill can be minimized.

20 In a process configuration, the solution can be placed in connection with the existing combustion of concentrated odorous gases, whereby so-called tail gases can be combusted in the existing equipment, such as in a soda recovery boiler, an odorous gas boiler, a lime sludge reburning kiln or a flame.

25 In the method according to the invention, it is preferable to use for the condensation of sulphur, e.g., the condenser water or the boiler water of the pulp mill.

In the arrangement according to the invention, the burning device of the Claus system, i.e.
the reactor, and a corresponding steam boiler is connected at its inlet to the odorous gas
30 line of the cooking department or the evaporation plant of the sulphate process or a corresponding source of odorous gas, and the concentrated odorous gases obtained therefrom can be combusted, in accordance with the principles of the Claus process, with substoichiometric amount of air to oxidize the sulphur compounds. To condensate the oxidation products obtained from the combustion device, the arrangement further

comprises a condenser, which can be used to condensate the products, the elemental sulphur in particular, into a liquid or solid form. In order to discharge these liquid or solid substances, the combustion device is equipped with a discharge assembly that is connected to the condenser. In addition, the unit further comprises an exhaust assembly for gaseous (uncondensed) bodies, which can be used to remove any light oxidation products, as well as inert and not reacted compounds (TRS and SO₂). As indicated in detail in the following, at least part of the sulphur compounds of the concentrated odorous gases coming from the Claus combustion are conducted to conventional odorous gas combustion which takes place in the soda recovery boiler, odorous gas boiler, lime sludge reburning kiln or flame, or in more than one of these devices. Therefore, the outlet of the gaseous compounds of the arrangement is preferably connected by means of pipe lines to the inlet of the soda recovery boiler or the lime sludge reburning kiln, or to a similar post-processing device.

In a process configuration, the solution can be placed in connection with the existing combustion process of concentrated odorous gases, whereby the so-called tail gases can be combusted in the existing equipment, such as in a soda recovery boiler or lime sludge reburning kiln or similar equipment, and the required condenser of sulphur on the cooling water side can be integrated into the water circulations/recovery of heat of the mill. In that case, the equipment solution is reduced into a simple and economic form. The solution according to the invention can be applied both to existing and new mills.

As a simple addition, the solution is particularly well suited for mill concepts, wherein the soda recovery boiler is the primary place of combustion of concentrated odorous gases.

In the following, the invention is examined more closely by means of a detailed description with reference to the appended drawings.

Fig. 1 shows a flow chart illustrating the collection of odorous gases.

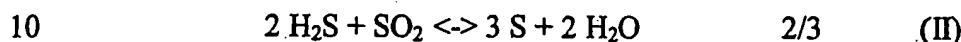
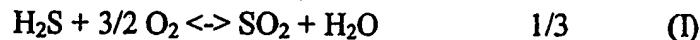
Fig. 2 shows, again with the aid of a flow chart, the processing method of odorous gases according to prior art.

Fig. 3 shows the recovery of sulphur by means of the Claus process, according to the invention.

Fig. 4 shows the flow chart of an alternative embodiment of the invention, wherein several burning devices of the Claus system are connected in parallel.

Fig. 5 shows the recovery of sulphur by means of the Claus process and the flow chart of the post processing of the gases from the Claus system.

One special feature of the invention is that the so-called Claus process is used to binding 5 sulphur from concentrated odorous gases. The following reactions take place in the Claus process:



The concentrated odorous gases are combusted with a substoichiometric quantity of air or oxygen, whereby part of the sulphur of the concentrated odorous gases remains elemental sulphur and part is combusted to sulphur dioxide. The amount of elemental sulphur 15 remaining is 50 to 90 molecular percent, typically 70 to 85 molecular percent.

The concentrated odorous gases herein refer to the smelly gases of the pulp mill, the concentration of which exceeds the so-called upper explosion limit. These gases consist of hydrogen sulphide, methyl mercaptan, and dimethyl sulphide and dimethyl disulphide, 20 among others.

The reduced sulphur in the concentrated odorous gases is enough concentrated, is also sodium-free and has a sufficiently rich thermal capacity. By burning at a suitable air index, the main part of the sulphur can be oxidized into elemental sulphur, as is the case in the 25 above conventional Claus process. The sulphur can be condensed and discharged separately as liquid sulphur, which is an inert chemical element with an inherent market value. The "air index" herein refers to the molecular proportion of oxygen (O_2) in the air to the sulphur (S) in the substance being treated. The air index is one, when the amount of oxygen in the air is in a stoichiometric proportion to the amount of sulphur of the gas to be 30 treated to change all the sulphur into sulphur dioxide. "Substoichiometric amounts of air", in turn, means that the air index is smaller than one.

In the present invention, the odorous gases are combusted with under air or short air, typically, at an air index of 0.4 – 0.9, whereby the adiabatic combustion temperature is

about 1400 - 1800°C. For one gas mixture, the combustion was carried out at an air index of about 0.6, whereby the adiabatic combustion temperature was about 1600°C.

According to one preferred embodiment of the invention the combustion of concentrated
5 odorous gases is carried out in adiabatic conditions at the temperature of 1400 - 1800°C.

According to the invention, part of the collected odorous gases are conducted to Claus
combustion and part of the sulphur compounds from the Claus combustion are conducted
to conventional odorous gas combustion, or optionally part of the collected odorous gases
10 are conducted directly to conventional odorous gas combustion.

More specifically, according to the method of the invention, the flow of odorous gases
collected from the source of concentrated odorous gases is conducted to combustion in a
first combustion unit, using the Claus process, through appropriate pipe lines, and the flow
15 of gases from the first combustion unit through appropriate pipe lines to a second
combustion unit, such as the odorous gas boiler, soda recovery boiler, lime sludge
reburning kiln or flame, or to more than one of these devices. Alternatively, part of the
flow of concentrated odorous gases can be conducted directly past the first combustion unit
and into the second combustion unit.

20 According to the invention, at least 10 molar percent of the collected odorous gases are
conducted to combustion in the first combustion unit using the Claus process. 30 – 90
molar %, typically 50 – 90 molar %, are preferably conducted through the Claus process.
The rest of the collected odorous gases, 10 – 90 molar %, can be conducted directly to
25 combustion in the existing apparatuses.

The concentrated odorous gases are combusted in the first combustion unit with
substoichiometric amounts of air. The sulphur that has oxidized into elemental sulphur is
condensed with the condenser and discharged in a molten form through the bottom of the
30 odorous gas combustion unit. The elemental sulphur in liquid form is conducted into the
collector and taken further to a means of transport. When cooling, liquid sulphur solidifies;
however, short storage for reuse in particular should be implemented in liquid form.

When necessary, the exhaust gases or tail gases are conducted into the second combustion unit of the Claus system to maximize the desulphurization. If required, the running conditions used in the latter combustion device may differ from those in the first combustion device.

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The exhaust or tail gases, such as sulphur dioxide and TRS, which come from the Claus system, are lead into at least one combustion device of the second combustion unit, such as the odorous gas boiler, soda recovery boiler, lime sludge reburning kiln or flame, to be disposed of. In this method, the Claus system is not intended for a complete recovery of 10 sulphur as elemental sulphur; on the contrary, at least 10 molecular percent of the sulphur compounds taken through the Claus system are taken to be combusted in the combustion device of the second combustion unit. Typically, at least 10 molecular percent, about 50 molar % at a maximum, preferably about 15 to 30 molar % of the sulphur compounds of the concentrated odorous gases coming from the Claus combustion are lead to combustion 15 in conventional combustion systems, such as soda recovery boiler or lime sludge reburning kiln.

The method according to the invention functions without catalysts. When necessary, the Claus system uses technology, such as catalysts, which was developed in connection with 20 the Claus combustion of hydrogen sulphide. Examples of suitable catalysts are cited in the published FI Patent Application No. 904949 or FI Patent Specification No. 102250.

The elemental sulphur obtained according to the method can be stored in a liquid or solid form and further transported in a liquid or solid form, for example, to a sulphuric-acid 25 plant or another pulp mill. It can also be recycled into the process, e.g., by suitably adding to white liquor (the manufacture of a polysulphide solution) or, when necessary, by feeding upstream into the soda recovery boiler by means of a combination burner or in some other way to adjust the sulphidity. As it is easy to store and transport, the recovery of sulphur in a liquid or solid form is advantageous.

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According to an alternative solution, the odorous gases can be combusted in a Claus reactor with the aid of oxygen instead of air.

According to a second alternative solution, the elemental sulphur can further be combusted to sulphur dioxide or processed to form sulphuric acid. Also in that case, however, the elemental sulphur can first be recovered by means of the combustion unit of the Claus process.

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According to a third alternative solution of the invention, the amount of concentrated odorous gases is increased, for example, by means of thermal treatment of black liquor.

In the following, the method according to the invention is examined with reference to the
10 appended figures.

Fig. 1 shows a flow diagram of the collection of concentrated odorous gases into the collectors of a cooking department 1 or an evaporator plant 2 from known sources of concentrated odorous gases either separately or in combinations thereof, using known
15 methods.

Fig. 2 shows a flow diagram of a prior art processing method of odorous gases, wherein the concentrated odorous gases are lead into an odorous gas boiler 3 (containing a condenser 7), soda recovery boiler 4, lime sludge reburning kiln 5 or flame 6, or into more than one
20 of them.

Fig. 3 shows the arrangement according to the invention suitable for the combustion of odorous gases. The arrangement according to the invention comprises at least one odorous gas combustion unit 10 (a first combustion unit), which a flow of concentrated odorous
25 gases can be collected in and lead into from a source of concentrated odorous gases, and wherein the reduced sulphur contained in the concentrated odorous gases can be combusted. The combustion unit comprises at least one combustion device 10 of the Claus system, and a condenser 11 connected thereto, and an air feeding assembly 18. The combustion unit is provided with a feeding assembly 14, which is connected to the source
30 of concentrated odorous gases, and an exhaust assembly 15, through which the oxidized and condensed sulphur compounds of the concentrated odorous gases can be discharged from the device as elemental sulphur in a liquid or solid form. The elemental sulphur can be lead into a collector 12 and further to a transporter 13. The combustion unit also comprises an exhaust assembly 16, through which the gaseous, uncondensed sulphur

compounds coming from the first combustion unit can be lead into the second combustion unit to be combusted. Furthermore, the feeding assembly 14 of the first combustion unit can be connected to a distribution piece 17 so that part of the concentrated odorous gases can be lead through the distribution piece and past the first combustion unit directly into
5 the second combustion unit to be combusted.

The second combustion unit comprises at least one combustion device, such as an odorous gas boiler, soda recovery boiler, lime sludge reburning kiln and/or flame.

10 Fig. 4 shows an arrangement, wherein the first combustion unit comprises at least two combustion devices 20, 21 of the Claus system, connected in parallel, and condensers 22, 23 connected thereto, and air feeding nozzles 33, 34. The combustion unit is provided with a feed nozzle 26, which is connected to the source of concentrated odorous gases, and with an exhaust nozzle 27, through which the oxidized and condensed sulphur compounds of
15 the concentrated odorous gases can be discharged from the device as elemental sulphur in a liquid or solid form. The elemental sulphur can be lead into a collector 24 and further to a transporter 25. The combustion unit also comprises an exhaust assembly 28, through which the gaseous, uncondensed sulphur compounds coming from the first combustion unit can be lead into the second combustion device 21 of the Claus system through a feeding
20 assembly 29. The latter combustion device 21 is provided with an exhaust assembly 32, through which the oxidized and condensed sulphur compounds can be discharged from the device as elemental sulphur in a liquid or solid form. The elemental sulphur can be lead into the collector 24 and further to the transporter 25. The second combustion device of the
25 Claus system is further provided with an exhaust assembly 30, through which the gaseous, uncondensed sulphur compounds coming from the combustion device of the Claus system can be lead into the second combustion unit to be combusted.

The feed nozzle 26 of the first combustion unit can be connected to the distribution piece 31 so that part of the concentrated odorous gases can be lead through the distribution piece
30 and past the first combustion unit directly into the second combustion unit to be combusted. Alternatively, the exhaust nozzle 28 of the first Claus combustion device of the Claus system can also be connected to the distribution piece, through which part of the gas stream from the first Claus combustion device can be lead directly into the second combustion unit to be combusted.

Fig. 5 shows the recovery of sulphur by means of the Claus process, wherein several Claus combustion devices are connected sequentially, and the flow diagram of the post processing of the gases from the Claus system. The arrangement comprises a first 5 combustion unit having at least two combustion devices 40, 41 of the Claus system connected in parallel, and condensers 42, 43 connected thereto, and air feeding assemblies 58, 59. The first combustion device of the Claus system is provided with a feed nozzle 46, which is connected to the source of concentrated odorous gases, and with an exhaust nozzle 47, through which the oxidized and condensed sulphur compounds of the 10 concentrated odorous gases can be removed from the device as elemental sulphur in a liquid or solid form. The elemental sulphur can be lead into a collector 44 and further to a transporter 45. The combustion device also comprises an exhaust nozzle 48, through which the gaseous, uncondensed sulphur compounds from the first combustion device of the Claus system can be lead into the second combustion device 41 of the Claus system 15 through a feeding nozzle 49. The latter combustion device 41 is provided with an exhaust nozzle 57, through which the oxidized and condensed sulphur compounds can be removed from the device as elemental sulphur in a liquid or solid form. The elemental sulphur can be lead into the collector 44 and further to the transporter 45. The second combustion unit of the Claus system is further provided with an exhaust nozzle 50, through which the 20 gaseous, uncondensed sulphur compounds coming the combustion device of the Claus system can be lead into the second combustion unit to be combusted.

As described in connection with Fig. 4, the feed nozzle assembly 46 of the first combustion unit can be connected to the distribution piece 51 so that part of the concentrated odorous 25 gases can be lead through the distribution piece and past the first combustion unit directly into the second combustion unit to be combusted. Alternatively, the exhaust nozzle 48 of the first Claus combustion device of the Claus unit can be connected to the distribution piece, through which part of the gas stream coming from the first Claus combustion device can be lead directly into the second combustion unit to be combusted.

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The exhaust or tail gases, such as sulphur dioxide and TRS, coming from the combustion device 41 of the Claus system of the first combustion unit, are lead to be disposed of in at least one combustion device of the second combustion unit, such as the odorous gas boiler

53 (which is provided with a condenser 52), soda recovery boiler 54, lime sludge reburning kiln 55 and/or flame 56.